

# PATENT SPECIFICATION

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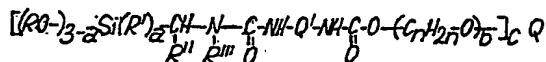
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## (54) SILYL-SUBSTITUTED UREA DERIVATIVES

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen 301, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain new silyl-substituted urea derivatives. These compounds can be regarded as carbamate-modified urea derivatives.

The invention provides organo-silanes of the general formula



in which

R is an alkyl or cycloalkyl radical with up to 6 carbon atoms or a phenyl radical, R' is an optionally halo- or cyano-substituted alkyl, cycloalkyl or aryl radical with up to 10 carbon atoms,

R'' is a hydrogen atom or a methyl or phenyl radical,

R''' is a hydrogen atom or an optionally halo- or cyanosubstituted alkyl, cycloalkyl or aryl radical with up to 10 carbon atoms,

Q' is an alkylene radical with 2 to 10 carbon atoms, a cycloalkylene, arylalkylene, arylene or alkylarylene radical with up to 10 carbon atoms, or is the radical  $-C_6H_4-CH_2-C_6H_4-$ ,

Q is a monovalent to hexavalent saturated aliphatic hydrocarbon radical with up to 6 carbon atoms,

a is 0, 1, 2 or 3,

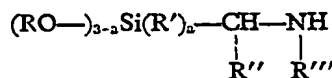
n is 2, 3 or 4,

b is zero or an integer from 1 to 200,

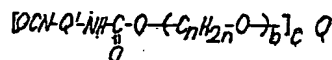
c is the valency number of Q.

The meaning of the symbols may of course vary within the ranges expressed above in each position of a molecule.

The invention also provides a process for the preparation of these compounds in which an aminoalkyl-silane derivative of the formula



is reacted with an isocyanate-modified carbamic acid ester of the formula



[Price 25p]

at a temperature of from  $-20$  to  $150^{\circ}\text{C}$ , preferably  $20$  to  $60^{\circ}\text{C}$ , optionally in the presence of a diluent.

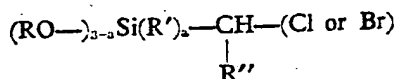
In general, this reaction is exothermic; if necessary, it may be moderated by cooling or, if it slows down, its completion may be accelerated by heating. Suitable diluents are inert solvents, such as cyclohexane or toluene, as well as alcoholic hydroxyl compounds, including those of high molecular weight, and mixtures of these types. The hydroxyl compounds can be used for diluting because, as is known, isocyanates react substantially faster with amines than with alcohols. If the diluent is a non-volatile high molecular weight hydroxyl compound, in particular, for example, a polyalkylene glycol monoalkyl ether of the formula



it is often of advantage to retain this polyether in the reaction product. If, on the other hand, a volatile solvent has been used for diluting, this is normally removed from the reaction product by distillation, in some cases advantageously in a thin layer evaporator.

The new products are suitable for use as intermediate layers imparting adhesion to siliceous surfaces which are to be coated with synthetic materials, as interface-active agents and as intermediates for the preparation of organo-polysiloxane resins. Their urea as well as their carbamate groupings impart to them a certain polarity and, in comparison with the non-functional organo-silicon compounds, give rise to a reduction of the sometimes disadvantageous solubility in non-polar solvents. Moreover, their viscosity is comparatively high by reason of the urea grouping, and this is desirable for some organo-polysiloxane resins.

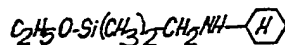
The aminomethyl-silane derivatives used for the preparation of the new compounds may be obtained according to a known method by reacting a chloro- or bromomethylsilane derivative of the formula



with an amine of the formula  $\text{R}'''\text{NH}_2$  at a temperature of from  $20$  to  $150^{\circ}\text{C}$ , preferably  $50$  to  $120^{\circ}\text{C}$ . It is advantageous to choose primary amines with boiling points above  $40^{\circ}\text{C}$ , such as cyclohexylamine or isobutylamine, which are preferably used in a five- to ten-fold excess and may then serve as a component of the reaction product to be obtained and, at the same time, as acid-binder and diluent.

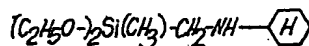
For example, the aminomethyl-silane derivatives used in the following Examples can be prepared as follows:

(A)  $394$  g (2 mols) dimethyl-(bromomethyl)-ethoxy-silane are added with stirring to  $992$  g (10 mols) cyclohexylamine, whereupon the temperature rises to about  $100^{\circ}\text{C}$ . The reaction mixture is subsequently heated at boiling temperature under reflux for 2 hours, and the precipitated amine salt is filtered off after cooling. By fractional distillation of the filtrate there is obtained, at  $18$  mm Hg between  $115$  and  $118^{\circ}\text{C}$ , the N-cyclohexyl-(aminomethyl)-dimethyl-ethoxy-silane of the formula



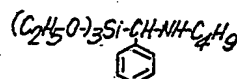
(B)  $356$  g (3.6 mols) anhydrous cyclohexylamine are heated to  $45^{\circ}\text{C}$  and  $136$  g (0.6 mol) methyl-(bromomethyl)-diethoxy-silane are gradually added in such a manner that a temperature of between  $60$  and  $70^{\circ}\text{C}$  is maintained. The mixture is then heated at  $100^{\circ}\text{C}$  for a further hour and then filtered at room temperature. By

fractional distillation of the filtrate there is obtained, a 14 mm Hg between 130 and 133°C, the N-cyclohexyl-(aminomethyl)-methyl-diethoxy-silane of the formula



and of refractive index  $n_D^{20}=1.4460$ .

- 5 (C) 103.5 g (0.31 mols)  $\alpha$ -bromobenzyl-triethoxy-silane which can be prepared in known manner by bromination of benzyl-trichlorosilane and subsequent ethanolysis  
10 are added dropwise at about 60°C to 136 g (1.86 mols) *n*-butylamine. The reaction mixture is then heated at boiling temperature under reflux for a further 3 hours and freed from the excess amine by reducing the pressure to 15 mm Hg and heating up to 80°C. The residue is dissolved in 100 ml anhydrous cyclohexane, the precipitated butyl ammonium bromide is filtered off, and by fractional distillation there is obtained, at 0.03 mm Hg between 100 and 105°C, the  $\alpha$ -(butylamino)-benzyl-triethoxy-silane of the formula



- 15 as a colourless liquid of refractive index  $n_D^{20}=1.4705$ .

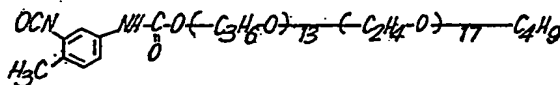
The isocyanate-modified carbamic acid esters are likewise obtained according to processes by reacting diisocyanates, e.g. toluylene-diisocyanate-(2,4) or hexamethylene diisocyanate, with hydroxyl compounds of the formula



- 20 The diisocyanate is preferably used in a substantial excess so that the number of OCN groups in the initial reaction mixture amounts to two to six times the number of HO groups, and the diisocyanate remaining at the end of the reaction is removed by distillation, advantageously in a thin layer evaporator.

- 25 The isocyanate-modified carbamic acid esters used in the following Examples can be prepared in the following way:

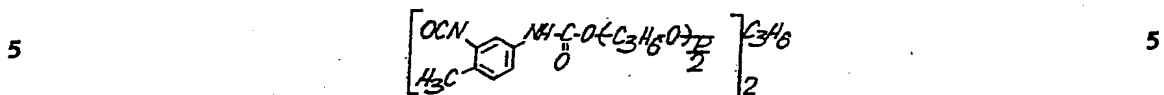
- 30 (1) 3000 g of an anhydrous polyalkylene glycol monobutyl ether which has been prepared in known manner by alkoxylation of 1 mol *n*-butanol first with 17 mols ethylene oxide and then with 13 mols propylene oxide and the molecular weight of which amounts, on average, to 1550 g, are mixed at 20 to 25°C with 1740 g (10 mols) toluylene-diisocyanate-(2,4) and the mixture is heated at 70°C for 5 hours. The reaction product is then freed from the excess toluylene diisocyanate by thin layer distillation at 0.1 to 0.2 mmHg and 150°C; if necessary, this is repeated. As residue there is obtained, without substantial loss of yield, a pale yellow oil the structure of which corresponds to the formula



Its content of OCN groups amounts to 2.62 per cent by weight, its molecular weight accordingly to 1605 g on average.

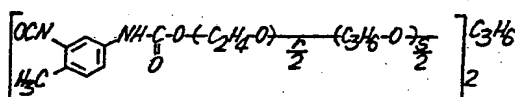
- (2) 1000 g of a polypropylene glycol which has been prepared in known manner by alkoxylation of 1 mol 1,2-dihydroxy-propane with 28.4 mol propylene oxide and the

molecular weight of which amounts, on average, to 2000 g, are mixed with 522 g (3 mols) toluylene-diisocyanate-(2,4), and the mixture is heated at 70°C for 6 hours. The reaction mixture is then freed from the excess tolylene diisocyanate in a thin layer evaporator at 0.2 mm Hg and 150°C. The residue corresponds to the formula



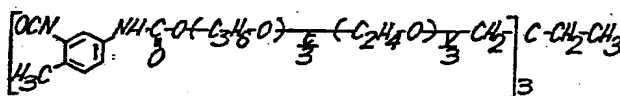
with *p*, on average, equal to 28.4. Its content of OCN groups amounts to 3.75 per cent by weight, its equivalent weight accordingly to 1120 g.

- 10 (3) 1500 g of a polyalkylene glycol which has been prepared in known manner by alkoxylation of 1 mol 1,2-dihydroxy-propane first with 59.8 mol propylene oxide and then with 11.6 mol ethylene oxide and the molecular weight of which amounts to 4000 g, are mixed at room temperature with 522 g (3 mols) toluylene-diisocyanate-(2,4), and the mixture is heated at 70°C for 6 hours. The reaction mixture is then freed from the excess toluylene diisocyanate in a thin layer evaporator at 0.1 to 0.2 mm Hg and 150°C. As residue there is obtained a clear pale yellow oil corresponding to the formula 15



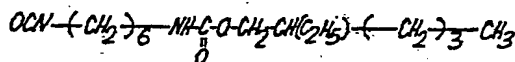
with *r*, on average, equal to 11.6 and *s*, on average, equal to 59.8. Its content of OCN groups amounts to 2.1 per cent by weight, its equivalent weight to 2000 g.

- 20 (4) 1000 g of a trihydroxy-polyether which has been prepared in known manner by alkoxylation of 1 mol 1,1,1-trimethylol-propane first with 7.5 mol ethylene oxide and then with 53 mol propylene oxide and the molecular weight of which amounts, on average, to 3430 g, are mixed at room temperature with 348 g (2 mols) toluylene-diisocyanate-(2,4), and the mixture is heated at 70°C for 6 hours. The reaction product is then freed from the excess toluylene diisocyanate in a thin layer evaporator at 0.1 to 0.2 mm Hg and 150°C. As a residue there is obtained a pale yellow oil the structure of which corresponds to the formula 25



- 30 with *t*, on average, equal to 53 and *v*, on average, equal to 7.5. Its content of OCN groups amounts to 3.35 per cent by weight, its equivalent weight accordingly to 1255 g. 30

- 35 (5) 130 g (1 mol) 2-ethyl-hexanol are added dropwise with stirring at 80 to 90°C to 1008 g (6 mols) hexamethylene diisocyanate, and the mixture is kept at 80°C for a further 5 hours. It is then freed from the excess diisocyanate in a thin layer evaporator at 0.3 mm Hg and 150°C. There remains a clear pale yellow liquid of low viscosity, the structure of which corresponds to the formula 35

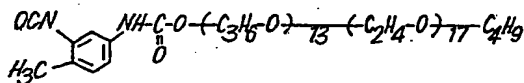


the content of OCN amounting to 15 per cent by weight.

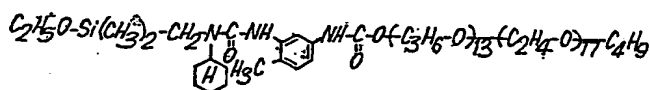
The following Examples are given for the purpose of illustrating the present invention:

#### EXAMPLE 1

161 g (0.1 mol) of an isocyanate-modified carbamic acid ester of the formula



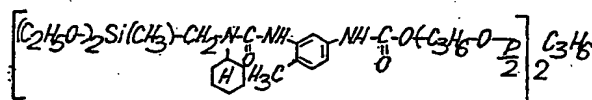
are mixed with 21.5 (0.1 mol) N-cyclohexyl-(aminomethyl)-dimethyl-ethoxy-silane, and the mixture is stirred for 20 hours; the temperature temporarily rises to 45°C. The product present at the end of the reaction is a pale yellow, clear, viscous oil which is soluble in water and has a structure corresponding to the formula



(I)

#### EXAMPLE 2

112 g (0.1 gram equivalent) of an isocyanate-modified carbamic acid ester as described above under (2) are mixed with 24.5 g (0.1 mol) N-cyclohexyl-(aminomethyl)-methyl-diethoxy-silane, and the mixture is stirred at room temperature, first under atmospheric pressure for one hour, then at 0.5 mm Hg for 30 minutes for degassing. The remaining product corresponds to the formula

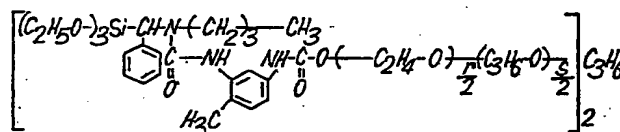


(II)

with  $p$ , on average, equal to 28.4.

#### EXAMPLE 3

200 g (0.1 gram equivalent) of an isocyanate-modified carbamic acid ester as described above under (3) are mixed with 32.5 g (0.1 mol)  $\alpha$ -(*n*-butylamino)-benzyl-triethoxy-silane, and the mixture is stirred at room temperature first under atmospheric pressure for one hour, then at 0.5 mm Hg for another hour for degassing. There remains a clear, thinly liquid, pale-yellow oil, the structure of which corresponds to the formula

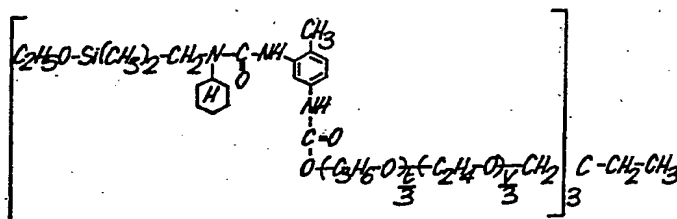


(III)

with  $r$ , on average, equal to 11.6 and  $s$ , on average, equal to 59.8.

#### EXAMPLE 4

253 g (0.2 gram equivalent) of an isocyanate-modified carbamic acid ester as described above under (4) are mixed with 43 g (0.2 mol) N-cyclohexyl-(aminomethyl)-dimethyl-ethoxy-silane, and the mixture is stirred for 3 hours; the temperature initially rises to about 40°C. The reaction mixture is then degassed at room temperature by reducing the pressure to 0.1 to 0.5 mm Hg for one hour. There remains a clear pale yellow oil the structure of which corresponds to the formula

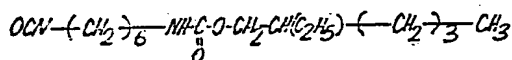


(IV)

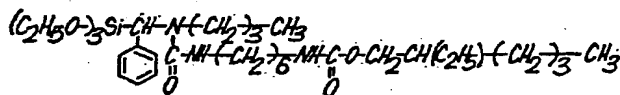
with  $t$ , on average, equal to 53 and  $\tau$ , on average, equal to 7.5.

## EXAMPLE 5

27.9 g (0.1 gram equivalent) of an isocyanate-modified carbamic acid ester of the formula

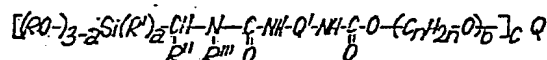


are gradually added to 32.5 g (0.1 mol)  $\alpha$ -(butylamino)-benzyl-triethoxy-silane, while cooling with ice, the mixture is stirred for 30 minutes, and there is obtained a clear viscous, almost colourless liquid of a structure substantially corresponding to the formula



## WHAT WE CLAIM IS:—

1. Silyl-substituted urea derivatives of the general formula



15 in which

R is an alkyl or cycloalkyl radical with up to 6 carbon atoms or a phenyl radical,  
R' is an optionally halo- or cyano-substituted alkyl, cycloalkyl or aryl radical  
with up to 10 carbon atoms,

R'' is a hydrogen atom or a methyl or a phenyl radical,

20 R''' is a hydrogen atom or an optionally halo- or cyano-substituted alkyl, cyclo-  
alkyl or aryl radical with up to 10 carbon atoms,

Q' is an alkylene radical with 2 to 10 carbon atoms, a cycloalkylene, arylalkylene,  
arylene or alkylarylene radical with up to 10 carbon atoms, or is the radical  
—C<sub>6</sub>H<sub>4</sub>—CH<sub>2</sub>—C<sub>6</sub>H<sub>4</sub>—,

25 Q is a monovalent to hexavalent saturated aliphatic hydrocarbon radical with  
up to 6 carbon atoms,

a is 0, 1, 2 or 3,

n is 2, 3 or 4,

b is zero or an integer from 1 to 200,

30 c is the valency number of Q.

2. The compound of the formula (I).

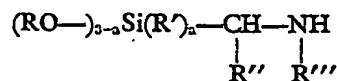
3. The compound of the formula (II).

4. The compound of the formula (III).

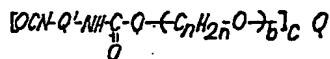
5. The compound of the formula (IV).

35 6. The compound of the formula (V).

7. A process for the production of silyl-substituted urea derivatives according to claim 1 in which an amino-alkyl-silane derivative of the formula



is reacted with an isocyanate-modified carbamic acid ester of the formula



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at a temperature from  $-20$  to  $150^\circ\text{C}$ .

8 A process according to claim 7 in which the reaction is carried out at  $20$  to  $60^\circ\text{C}$ .

9. A process according to claim 7 or 8 in which the reaction is carried out in the presence of a diluent.

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10. A process according to claim 9 in which the diluent is one of those hereinbefore mentioned.

11. A process for the production of a compound according to claim 1, substantially as hereinbefore described in the Examples.

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12. Silyl-substituted urea derivatives whenever prepared by a process according to any of claims 7—11.

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